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**Citation for published version:**

Knapp, CE, Carmalt, CJ, McMillan, PF, Wann, DA, Robertson, HE & Rankin, DWH 2008, 'Dimethylalkoxygallane incorporating a donor-functionalised alkoxide: the monomeric gas-phase structure' Dalton Transactions, no. 48, pp. 6880-6882. DOI: 10.1039/b817893n

**Digital Object Identifier (DOI):**

[10.1039/b817893n](https://doi.org/10.1039/b817893n)

**Link:**

[Link to publication record in Edinburgh Research Explorer](#)

**Document Version:**

Publisher's PDF, also known as Version of record

**Published In:**

Dalton Transactions

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# Dimethylalkoxygallane incorporating a donor-functionalised alkoxide: the monomeric gas-phase structure†

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Received 10th October 2008, Accepted 20th October 2008

First published as an Advance Article on the web 30th October 2008

DOI: 10.1039/b817893n

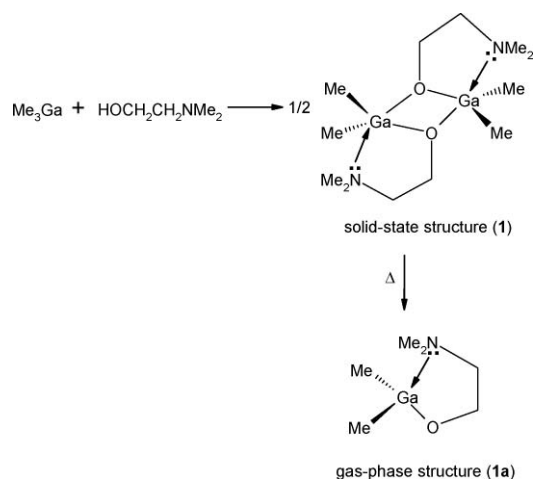
The structure of the vapour produced upon heating the dimethylalkoxygallane  $[\text{Me}_2\text{GaOCH}_2\text{CH}_2\text{NMe}_2]_2$  has been studied by gas-phase electron diffraction and *ab initio* molecular orbital calculations; only the monomeric form  $[\text{Me}_2\text{GaOCH}_2\text{CH}_2\text{NMe}_2]$  is observed in the vapour, with the nitrogen atom forming a dative bond with the metal centre.

Chemical vapour deposition (CVD) techniques are now widely employed for the deposition of thin films of materials because they offer the potential for good film uniformity and composition control, large area growth and excellent step coverage.<sup>1</sup> An important consideration when using the CVD method is the choice of precursor, as this can affect the growth rate, conformality, electrical properties, and transparency of the film.<sup>2</sup> However, information on the mechanisms of the CVD process, including how the precursors decompose, which species are present in the gas phase and the chemical reactions that are involved, is often limited.<sup>3,4</sup>

The versatile nature of metal alkoxides as convenient precursors to metal oxides *via* CVD processes is widely recognised;<sup>5,6</sup> they are easy to prepare and purify and are intrinsically non-corrosive so can be stored almost indefinitely when kept in a dry atmosphere. Furthermore, metal alkoxides are ideal for use in aerosol-assisted (AA)CVD due to their solubilities in a wide range of organic solvents, and in low-pressure (LP)CVD as a result of their high volatilities.<sup>7</sup> However, in order to exploit the full potential of CVD it is sometimes necessary to tailor the properties of the precursor in order to optimise process parameters such as evaporation temperature, deposition temperature, layer purity and uniformity. We have been investigating the deposition of gallium<sup>8,9</sup> and indium<sup>10</sup> oxide thin films using alkoxide precursors<sup>11,12</sup> *via* both AACVD and LPCVD. We have shown previously that the replacement of simple alkoxide groups<sup>13</sup> by donor-functionalised alkoxides, such as dimethylamino ethoxide (dmae), can result in precursors with improved physical properties and enhanced CVD performance. For example, dmae provides an additional Lewis base site, which is able to form chelate rings and provide stabilisation to the metal centre.

Knowledge of the structures and natures of precursors in the gas phase should provide useful information regarding the decomposition processes central to CVD. However, despite the growing importance of gallium and indium oxides<sup>14</sup> in gas sensing and transparent conducting oxide (TCO) applications, little is known about the gas-phase structures of the alkoxide precursors used to deposit the films. Moreover, given the large variety of metal oxides (including main group, lanthanide and transition metal elements) deposited from metal alkoxides incorporating donor-functionalised ligands, an understanding of gas-phase structures could lead to improvements in precursor design and film growth.<sup>15</sup> Our interest in the development of alternative volatile precursors to a range of materials has led us to determine the gas-phase structure of a CVD precursor and hence obtain information on the chemical species present in the CVD process. Herein we describe the gas-phase electron diffraction (GED) structure of a molecular precursor to gallium oxide,  $[\text{Me}_2\text{GaOCH}_2\text{CH}_2\text{NMe}_2]_n$ , demonstrating that although this complex is dimeric in the solid state ( $n = 2$ ),<sup>16</sup> in the gas phase it exists solely as a monomer ( $n = 1$ ).

The dimethylalkoxygallane  $[\text{Me}_2\text{GaOCH}_2\text{CH}_2\text{NMe}_2]_2$  (**1**) was prepared from the reaction between  $\text{Me}_3\text{Ga}$  and  $\text{HOCH}_2\text{CH}_2\text{NMe}_2$  using a slightly modified version of the published route (Scheme 1).<sup>16</sup> The <sup>1</sup>H and <sup>13</sup>C NMR spectra of **1** confirmed the sample was pure to within the sensitivity of the spectrometer. The crystal structure of **1** has been reported previously,<sup>16</sup> and shown to adopt a dimeric structure, with a planar  $\text{Ga}_2\text{O}_2$  ring and each gallium atom coordinated with a distorted



**Scheme 1** Preparation of  $[\text{Me}_2\text{GaOCH}_2\text{CH}_2\text{NMe}_2]_2$  (**1**) and  $[\text{Me}_2\text{GaOCH}_2\text{CH}_2\text{NMe}_2]$  (**1a**).

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† Electronic supplementary information (ESI) available: Experimental details relating to the electron diffraction refinement, final GED Cartesian coordinates for **1a**, calculated Cartesian coordinates for **1a**. See DOI: 10.1039/b817893n

trigonal bipyramidal geometry (Scheme 1). The FTIR and mass spectra of **1** prepared in this work confirmed the formation of dimers.

*Ab initio* molecular orbital calculations were performed for both the dimeric and monomeric forms of  $[\text{Me}_2\text{GaOCH}_2\text{CH}_2\text{NMe}_2]_n$ . The calculations for the dimer indicated that in isolation it would have a structure generally similar to that seen in the crystalline state. The possibility of structures with both  $C_2$  and  $C_i$  point-group symmetries were considered and it was estimated that the structure with  $C_2$  symmetry would be lower in energy by approximately  $2.8 \text{ kJ mol}^{-1}$ . For the monomer, scans of the potential energy upon rotation about the O(5)–C(6) and C(6)–C(7) bonds (see Fig. 1 for atom numbering) were performed to investigate the presence, or otherwise, of different conformers. Only one structure representing a minimum on the potential-energy surface was identified ( $C_i$  symmetry), in which the gallium and nitrogen atoms come close together to form a five-membered ring through dative bonding.

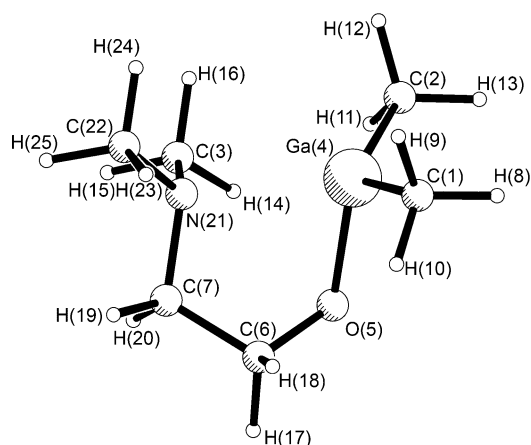


Fig. 1 Molecular structure of **1a** including the atom numbering scheme.

The relatively high volatility of **1** allowed a gas-phase electron-diffraction experiment to be performed by heating the sample to 398 K, with the nozzle heated to 415 K to prevent the sample recondensing. Analysis of the diffraction data revealed that the gaseous sample contained only the monomeric form **1a** with the geometry shown in Fig. 1. The fit of the theoretical model to the experimental data was relatively good, with  $R_G = 0.094$  ( $R_D = 0.069$ ), and can be visualised using the radial-distribution curve in Fig. 2, which shows the experimental curve and the experimental-minus-theoretical difference curve. If there had been a proportion of the dimeric form of **1** present in the gas-phase sample there would have been evidence for interatomic interactions at distances longer than about 6 Å.

Calculations were performed for the isolated monomer at HF/6-31G\*, MP2(full)/6-31G\* and MP2(full)/6-31G\* levels. The optimised structures reveal that **1a** is a very floppy molecule. For example, calculated values for the Ga–O–C(6)–C(7) dihedral angle have a range of more than  $12^\circ$  and for the O–C(7)–C(6)–N dihedral angle a range of  $6^\circ$ . Despite this, the highest level *ab initio* calculated structure of  $[\text{Me}_2\text{GaOCH}_2\text{CH}_2\text{NMe}_2]$  (**1a**) shows reasonably good agreement with the GED structure. Because the molecule has many degrees of flexibility, some of the

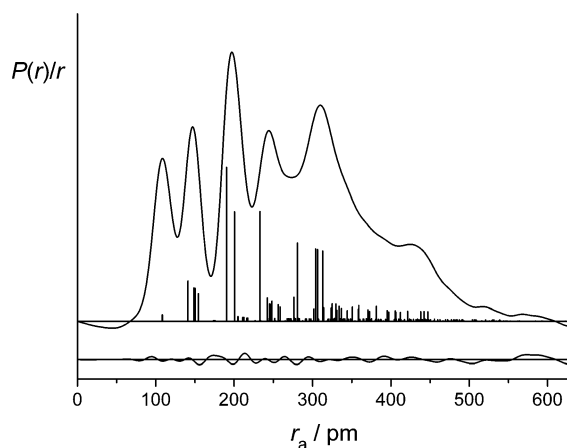


Fig. 2 Radial-distribution curve from the GED refinement of **1a**.

experimental estimated standard deviations for the torsion angles are large, typically  $2$  to  $3^\circ$ .

The Ga atom in the gas-phase structure of **1a** is surrounded by two methyl groups as well as one oxygen and one nitrogen atom derived from the aminoalkoxide chelate. The Ga atom therefore has a distorted tetrahedral arrangement, with the N(21)⋯Ga–X angles in the range  $81.6(10)$ – $107.9(19)^\circ$ . There is no indication of the formation of additional gallium-donor interactions (*i.e.* the presence of dimers) and hence the coordinative unsaturation of the Ga atom is satisfied by a dative interaction with the nitrogen atom in the gas phase.

The Ga⋯N distance in **1a** has been determined in the gas phase to be  $2.332(11) \text{ Å}$ . This can be compared to the solid-state structure, where the Ga⋯N bond distance was  $2.471(4) \text{ Å}$ .<sup>16</sup> This is a relatively large difference even considering the fact that two different methods have been applied. However, it is not surprising that the bond distance would be shorter in monomeric **1a** compared to dimeric **1**. The Ga–O bond distance in **1a** in the gas phase is  $1.906(4) \text{ Å}$ , which is similar to the equatorial Ga–O bond length of  $1.913(3) \text{ Å}$  in the solid state, but shorter than the axial Ga–O bond distance of  $2.078(3) \text{ Å}$ . The average Ga–O bond length for tetrahedrally and octahedrally coordinated gallium atoms is  $1.96 \text{ Å}$ .<sup>13,16</sup> For the dimeric structure **1**, the equatorial bonds would be expected to be shorter and axial ones longer based on hybridisation effects alone; this is indeed observed. The shorter Ga–O distance observed in gas phase **1a** is probably the result of monomer formation and the constraints of the chelating ring.<sup>17</sup>

This work has shown that compound **1** is monomeric in the gas phase. Therefore, although dialkylalkoxygallanes incorporating donor functionalised ligands generally adopt dimeric structures in the solid state, in the gas phase monomers are likely to be present. Monomers are expected to exhibit enhanced volatility in comparison to oligomeric complexes in which intermolecular solid-state interactions are likely to increase the enthalpy of vaporisation. However, this work shows that the structure adopted in the solid state may differ from that in the gas phase and so compounds that appear unsuitable for CVD may in fact be feasible precursors. Overall, this study has provided information that can be used when designing precursor molecules for a range of technologically important materials.

## Acknowledgements

We thank the EPSRC for funding the electron-diffraction research, including a visit by CEK to Edinburgh. The EPSRC are also thanked for a DTA award (CEK). The Edinburgh group is grateful to the National Service for Computational Chemistry Software for computing resources.

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